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MASS SPECTROMETER STUDY OF METAL-CONTAINING FLAMES

EIGHTH QUARTERLY TECHNICAL SUMMARY REPORT  
1 July - 30 September 1963

ARPA Order No. 23-62, Amendment No. 28  
Project Code No. 9100

M.R.I. Project No. 2551-P

For

Director  
Advanced Research Projects Agency  
Washington, D. C.



MIDWEST RESEARCH INSTITUTE

M I D W E S T   R E S E A R C H   I N S T I T U T E

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by

Thomas A. Milne

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## PREFACE

This report was prepared for the Advanced Research Projects Agency under ONR Contract No. Nonr-3599(00) monitored by Dr. Ralph Roberts and Mr. Roland Jackel of the Power Branch, ONR. The report describes the application of a high pressure molecular beam sampling system to pure gases, mixtures, and 1 atmosphere flames with additives.

The research staff consists of Dr. Thomas A. Milne, project leader, Dr. Frank T. Greene and Mr. George Vowels. Dr. Ronald Stearman has made many excellent comments about the effects in the supersonic flow of the first orifice, and Professor Paul W. Gilles of the University of Kansas has offered valuable comments on the sampling process.

Approved for:

MIDWEST RESEARCH INSTITUTE



Sheldon L. Levy, Director  
Mathematics and Physics Division

7 November 1963

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### SUMMARY

Studies with an aerodynamic molecular beam sampling system at 0.1 to 5 atmospheres show that the shape of the second orifice (skimmer) is unimportant when beam densities are low at the skimmer. With higher densities a blunt skimmer reduces polymer formation and increases mass separation effects. The drop-off in beam intensity with increasing orifice-to-skimmer distance does not disagree with the normal molecular beam scattering dependence. Changes and improvements in the sampling system to facilitate work with flames containing condensible species are described.

## I. INTRODUCTION

The first seven progress reports<sup>1/</sup> have described our work in developing a molecular beam sampling system for reactive systems at 1 atmosphere. These reports describe what we believe to be the major phenomena encountered in such sampling and present empirical studies on the behavior of the beam as a function of various parameters.<sup>1-3/</sup> Preliminary work on actual flames is also reported, including studies of the  $\text{Cl}_2$ -2Cl equilibrium in a  $\text{CO-O}_2$  flame<sup>1/</sup> and the various species observed when  $\text{BCl}_3$  is added to a  $\text{H}_2\text{-O}_2$  flame.<sup>2/</sup>

Two unusual phenomena have been observed and studied in sufficient detail to make first order corrections for them in actual flame equilibrium sampling experiments. These are the phenomena of "mass separation"<sup>3/</sup> and polymer or cluster formation.<sup>1/</sup>

During the past quarter our work has been mainly of a transition nature, in which we have been modifying the apparatus, adding improvements and studying a few remaining beam parameters all aimed at facilitating actual quantitative flame studies with metal additives which form condensible combustion products. In this report we describe (1) changes and planned improvements in the beam system, mass spectrometer detection system, and flame burners, (2) studies of beam behavior as a function of second slit (skimmer) geometry and of stage-one pressure, and (3) plans for future thermochemical studies in flames.

## II. BEAM FORMATION STUDIES

### A. Dependence of Sampling Behavior on Skimmer (Second Orifice) Geometry

The skimmers used previously have been made as sharp-edged as possible in order to minimize the aerodynamic interaction with the skimmer of the supersonic flow from the first orifice. These skimmers were made by simply forming a cone of apex angle  $60^\circ$  from 0.00035 in. thick nickel sheet. Although the 0.00035 in. skimmers were easily constructed, they were extremely fragile. When working with flames containing condensible products which plugged the first orifice, the skimmers were often damaged during the unplugging process. For this reason and also to add to our understanding of the process of beam formation, we studied various aspects of sampling behavior with three different skimmers.

In addition to the skimmer described above, a similar cone was formed from 0.002 in. stainless steel sheet. This skimmer was quite rugged and could be cleaned readily without damage. The third skimmer consisted of a 3/16 in. diameter flat disk, 0.002 in. thick, soldered onto the larger cone which held all skimmers. The diameter of the skimmer opening was approximately 0.010 in. in each case.

The beam behavior was compared for these skimmers as a function of several parameters and the results can be summarized as follows. The sharp conical skimmer and the 0.002 in. thick conical skimmer gave virtually identical results in all studies. The blunt skimmer - essentially a flat disk - departed significantly in behavior from the other two under certain conditions. Maximum beam intensity with the flat skimmer was comparable to that obtained with sharp skimmers at pressures of 0.1 atmosphere or lower, but dropped off markedly at 5 atmospheres. At all pressures, intensity dropped off with decreasing orifice-to-skimmer distance more rapidly than for sharp skimmers.

The two phenomena, mass separation and polymer formation, were studied for each skimmer. The use of the flat skimmer resulted in less polymers in the final beam at pressures above 100 Torr. At 5 atmospheres the dimer-to-monomer ratio in argon was reduced by a factor of 30. Again, the flat skimmer effect on polymers was most pronounced at small orifice-skimmer distances, 1/4 in. or less, and had little effect at 1/2 in. to 1 in. Mass separation in a 50-50 mixture of  $H_2$  and argon was studied for each skimmer. The separation was significantly enhanced with the flat skimmer at a pressure of 1 atmosphere and at small orifice-to-skimmer distances.

The above facts can be tentatively rationalized by noting that the flat skimmer behaves significantly differently from the sharp skimmers under two conditions, small orifice-skimmer distances and high pressures; that is, when the density of gas is high at the skimmer entrance. This high density would be expected to promote shock formation at the skimmer. A shock across the skimmer, in turn, would reduce beam intensities, destroy polymers formed earlier in the expansion, and perhaps lead to increased mass separation according to a recent postulate by Fenn.<sup>4/</sup>

#### B. Effect of Stage-One Pressure on Beam Intensity

The addition of a vacuum valve in the first stage pumping line, as described below, allowed us to investigate conveniently the effect of stage-one pressure,  $P_1$ , on beam behavior. With a 0.002 in. orifice and with the skimmer many orifice diameters downstream, beam intensity varied with  $P_1$  according to a simple molecular beam scattering law. In fact, the scattering

behavior at different orifice-to-skimmer distances was consistent with earlier scattering results obtained in stages two and three, where molecular flow certainly exists.

These results suggest that under such conditions the flow over most of the distance between the first orifice and the skimmer is essentially molecular flow. With larger first orifice diameters the slope of the scattering curves becomes less at a given orifice-skimmer distance, suggesting that the continuum-like flow operates over a greater part of the distance to the skimmer.

### C. Effect of Sampling-Orifice Diameter on Quenching

In discussions with Professor Gilles about the problem of quenching reactive equilibria in such high pressure sampling, he raised the question of the effect of first orifice size on quenching. If one considers qualitatively the history of the central core of gas as it expands to molecular flow from the first orifice, it becomes apparent that the time rate of expansion of the gas depends approximately linearly on the first orifice diameter. Thus, the collision history of the gas will change and the time available for shifting equilibria will increase as the diameter increases. This dependence, which it is hoped can be put on a quantitative kinetic basis from what is presently known about the beam formation process, can be very useful in checking on our ability to quench equilibria in systems of interest.

As a first check on such a dependence we have examined the monomer-to-dimer ratio in argon sampled with orifices of various diameters. Based on our picture of the origin of the dimer in such sampling it would be expected that more dimer would be formed with larger orifices, dissipative factors remaining the same. This was actually indicated in working with orifices from 0.002 in. to 0.020 in. diameter although the differing beam conditions were such that the observation is only qualitative. This aspect of sampling will be pursued further in flame quenching studies.

## III. CHANGES IN APPARATUS

In view of anticipated problems in working regularly with condensible species in flames, we have made several changes in our sampling system. The supporting system was rebuilt to allow more ready access to the first orifice and burner. At the same time a 6-in. vacuum valve was put in the pumping line to stage one permitting all diffusion pumps to be rapidly isolated for quick replacement or unplugging of orifices or skimmers.

The general hydrocarbon background from our sampler system is high enough to be troublesome at certain masses. The most general approach to overcome this as well as to eliminate any other nondirect beam contributions to the ion signal is to operate the beam in a pulsed or "AC" mode. Although several workers have utilized narrow band amplifiers and phase sensitive detection to obtain discrimination between the AC and DC components of the signal, we have designed a simpler and less expensive system using an alternate approach in which the signal with the beam on and off is fed into separate channels, integrated, and compared. We plan to use a mechanical chopper and a photodiode switching circuit. This system should be installed and tested during the next quarter.

A limited amount of effort during this past quarter has been devoted to improving our system for measuring flame temperatures. We have been concerned because our line reversal temperature measurements may be perturbed by the Na in the cooler outer layers of the flame. We have, therefore, constructed a sheathed, water-cooled, laminar flow burner which has provision for adding Na (and other metal compounds of interest) to the central portion of the flame only. The outer flame then acts as a shield, and ensures a constant temperature across the Na-containing portion of the flame. This type of burner will be used for all future studies of 1 atmosphere flames.

#### IV. LOW PRESSURE FLAMES

Some recent experiments, in which metals were added to flames, indicate that plugging at the sampling orifice may be a serious problem. The rate of plugging of the orifice can be reduced by making the orifice larger, but this is not possible with our limited pumping speed, unless the flame is operated at reduced pressures. At reduced pressures, however, the pressure of the species being studied is necessarily reduced due to both the drop in total pressure of additive and the mass action law. This can be partially compensated for by an increase in the size of the second orifice (skimmer), giving a more intense beam. Final analysis shows that for a typical equilibrium such as



at a total pressure of 76 Torr instead of 1 atmosphere, a net gain of 10 in the sensitivity for a given plugging rate can be expected.

The use of low pressure flames presents additional problems in temperature measurement, addition of metals, etc. However, they may be useful or even necessary for the study of some systems, and we have, therefore, built and operated a burner at 76 Torr with a  $C_2N_2$ -air flame. In particular, the use of lower pressures may help resolve questions about the ability to quench reactive and condensible species from flames since the quenching ability increases rapidly with lower initial pressures.

## V. FUTURE WORK

Studies will continue on sheathed burners, temperature measurements, effect of sampling probe on temperature, and methods of adding metals to 1 atmosphere flames. The low pressure burner will be used in looking for the free radicals O, OH, and H (so far not observed at 1 atmosphere) and checking the effect of pressure on quenching ability. The pulsed beam and detection system will be completed and tested. The dissociation equilibria of  $Cl_2$  and HCl will be quantitatively characterized as will stable products in CO- $O_2$  and  $H_2$ - $O_2$  flames. Work on known and unknown condensible species will be started to indicate the principal problems to be solved before studying two systems of primary interest, the  $Al_2O_3$ - $H_2O$  and the BeO- $H_2O$  systems.

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